Self-Organized MEH-PPV Domains in a TPU Matrix and the Consequences to the Luminescence Spectra

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ABSTRACT: Self-sustained cast films formed from heterogeneous blends of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) conjugated polymer and thermoplastic polyurethane (TPU) were investigated by photoluminescence (PL) and scanning electron microscopy (SEM). A blue shift is observed for the pure electronic transition PL peak (E_{00}) with decreasing MEH-PPV concentration. The two clear shoulders in the PL spectra at higher energy than the E_{00} peak appear due to the formation of small conjugation segments of the MEH-PPV molecules at the interface of the spherical MEH-PPV domains. This assumption and the origin of the blue shift were confirmed by correlating the average size of the MEH-PPV domains, observed from SEM images, and the analysis of the PL spectra at low temperatures. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3659–3664, 2008

Key words: conjugated polymer; optical properties; polymer blend; scanning electron microscopy; thermoplastic polyurethane

INTRODUCTION

Conjugated polymer materials represent an important alternative for technological applications in electronic and optoelectronic devices.[1–6] Besides, their photophysical properties[7–15] have been the subject of interest regarding the challenge of understanding complex structure versus property relationships. Blends of polymeric materials[16–22] are also a field of high interest. For the blends, the different aspects of the constituent polymeric materials can be combined to create new compounds with extended potential applications. As an example, blends[23,24] of MEH-PPV and PEO [poly(ethylene oxide)] are studied to correlate the morphological, electrical, and optical properties of the samples. In another application, PEO is also used as an insulating layer between the metal cathode and the polymeric active layer, which was responsible for significant improvement of efficiency and stability of light emitting diodes.[25] The control and a complete understanding of the additional properties of blends become, thus, of evident interest. In this work we perform an optical investigation, via photoluminescence (PL) measurements at different temperatures, to explain the different shapes of the PL spectra observed for the blended MEH-PPV/TPU self-sustained films at different concentrations of MEH-PPV in the TPU matrix. SEM images of the samples provided the necessary information, which have enabled us to correlate the morphological and the optical properties in a straight manner. This work has been performed with the main task to provide a further discussion about the contribution of the self-organization of MEH-PPV in separated domains and the arrangement of polymer segments at the interface of the domains to the shape of the PL spectra of the blends.

EXPERIMENTAL

The TPU ($M_w = 1 \times 10^5$ g mol^{-1}) was synthesized as described in Ref. 26. The MEH-PPV conjugated polymer was acquired from Aldrich, with an average weight molar mass of 55,000 g mol^{-1}. Blend solutions of MEH-PPV/TPU at 0.1, 0.5, 1.0, 5.0, 8.5, and 10.0 wt % concentrations of MEH-PPV were prepared by mixing the appropriate amounts of the corresponding polymers into tetrahydrofurane (THF) solvent and were subsequently stirred for 12 h. The
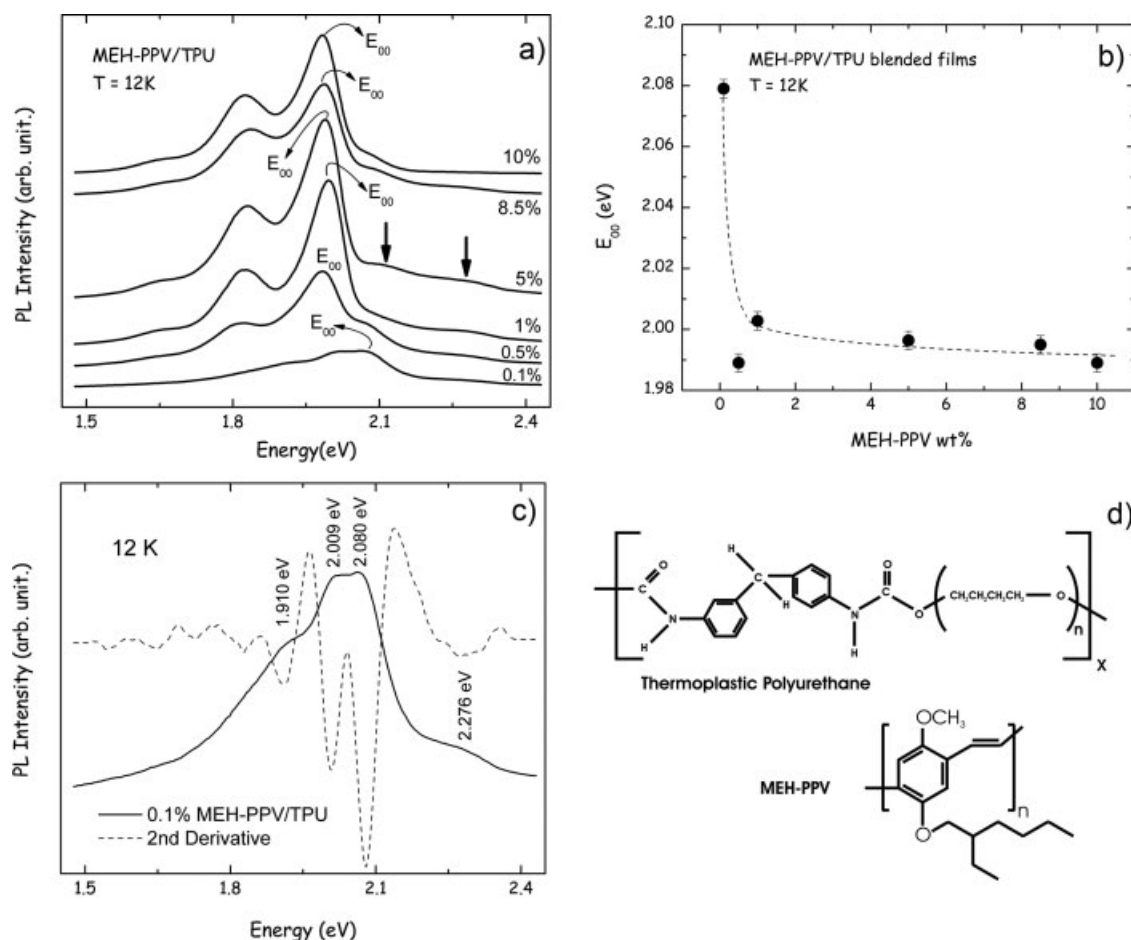
Figure 1 (a) Photoluminescence spectra at 0.1, 0.5, 1.0, 5.0, 8.5, and 10.0 wt % of MEH-PPV into the TPU matrix at 12 K. The arrows indicate the positions of the shoulders at the higher energy side of the spectra; (b) the behavior of the pure electronic transition energy peak (E_{00}) as a function of the MEH-PPV concentration in the TPU matrix. The dashed line is a guide for the eyes; (c) The PL spectrum for the 0.1 wt % blended film at 12 K and the corresponding minima of the second derivative curve (dashed line) showing the energies of the main features of the PL spectrum; (d) The monomeric units for the synthesized TPU and the MEH-PPV conjugated polymer.

amount of TPU used in each sample was 160 mg. The respective amounts of MEH-PPV for the 0.1, 0.5, 1.0, 5.0, 8.5, and 10.0 wt % blend concentrations were: 0.16, 0.80, 1.60, 8.00, 13.60, and 16.00 mg. Self-sustained films were obtained by casting the blend solution and drying under vacuum at room temperature for more than 1 week. The typical thickness of the self-sustained films were of the order of 500 μm. SEM images of the self-sustained films were obtained from a JEOL instrument, model 840A, for cryogenically-fractured surfaces.

The PL spectra for the self-sustained MEH-PPV/TPU films at different concentrations were measured at low temperatures with the samples under vacuum, inside a cold finger closed circuit cryostat to avoid any photo-oxidation effect. A CW Ar-ion laser emitting at 488.0 nm was used as the excitation source. The PL emission was collected in a backscattering configuration, focused into a JARREL-ASH

0.5 m monochromator, and detected by a gallium arsenide (GaAs) photomultiplier tube.

RESULTS AND DISCUSSIONS

The PL spectra at 12 K for the self-sustained films at different concentrations of MEH-PPV are shown in Figure 1(a). The E_{00} peak positions, as assigned in the Figure 1(a), correspond to pure electronic transition energies at each concentration. In Figure 1(b) the E_{00} energies are depicted as a function of MEH-PPV concentration. The positions were obtained from the corresponding minima of the second derivative. As an example, the PL spectrum for the blended film with 0.1 wt % of MEH-PPV at 12 K and its second derivative curve (dashed line) are shown in Figure 1(c). The monomeric units for the
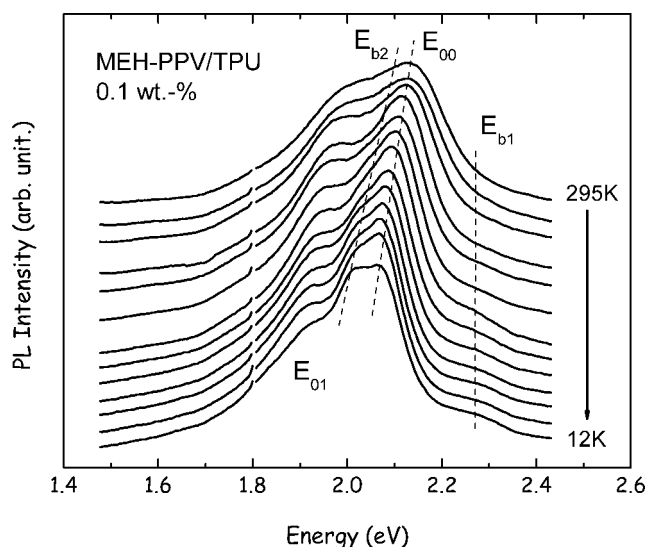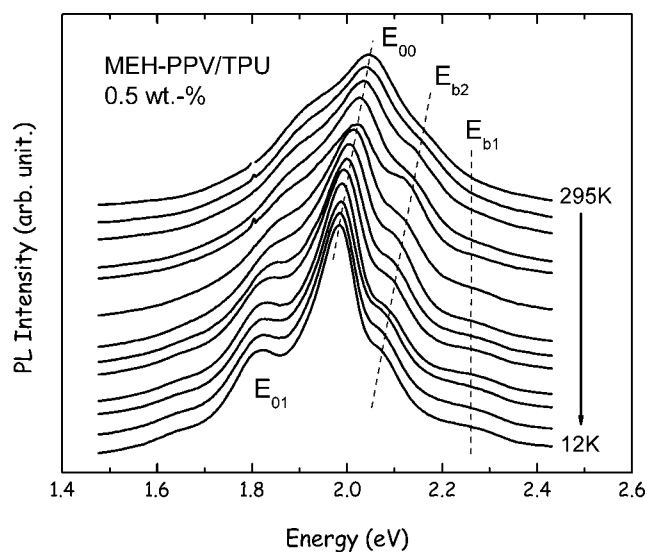
Figure 2 Sequence of PL spectra at different temperatures from 295 to 12 K for the self-sustained film at 0.1 wt %. The temperatures of the spectra are 295 K, 275 K down to 25 K in steps of 25 and 12 K. The dashed lines indicate qualitatively the change of the energy positions for the pure electronic transition peak E_{00} and for the shoulders E_{b1} and E_{b2}. The shoulder appearing around 1.9 eV is the first vibronic band E_{01}.

synthesized TPU and for the MEH-PPV conjugated polymer are shown in Figure 1(d).

Note in Figure 1(a) the presence of two shoulders on the higher energy side of the spectra (see arrows). Their relative intensity is lower than the intensity of the E_{00} peak. However, with decreasing MEH-PPV concentration the spectra displace to the higher energy side and the relative contribution of the shoulder closer to the E_{00} increases substantially [see Fig. 1(c), as an example]. The formation of the shoulders at higher energies is better seen from the complete sequence of spectra with decreasing temperature. In Figures 2 and 3 the evolution of the spectra is shown from 295 K down to 12 K for the blended self-sustained films at 0.1 and 0.5 wt % of MEH-PPV, respectively. The maximum PL intensity increases with decreasing temperature. This behavior is observed in all the samples. The ratio between the maximum PL intensities at 12 and 295 K obtained from the lower to the higher MEH-PPV concentration are respectively: 1.29 (0.1 wt %), 1.52 (0.5 wt %), 2.06 (1.0 wt %), 1.96 (5.0 wt %), 1.53 (8.5 wt %), and 2.05 (10.0 wt %). The shoulders were labeled as E_{b1} and E_{b2}. The dashed lines in Figures 2 and 3, indicate qualitatively the change of their respective energy positions. A dashed line for E_{00} is also depicted in Figures 2 and 3 as a reference. The shoulders E_{b1} and E_{b2} appear at higher energies than E_{00} for all samples, unless for the case at 0.1 wt %, where E_{b2} appears at lower energy than E_{00}. The

shoulder E_{b2} is interpreted as being the first vibronic emission from E_{b1}. Both shoulders are broadened and the second derivative can only give an estimative of their average positions. The E_{b1} shoulder does not change effectively with decreasing temperature. Its average position is $E_{b1} = (2.26 \pm 0.02)$ eV, while the change of E_{b2} is really visible. The change of E_{b2} with decreasing temperature (corresponding dashed lines in Figs. 2 and 3) can be in part explained due to the increase of the energy of the vibrational mode that is interacting with the π-electrons, as has been reported in our previous works.[14,27,28] The average energy difference $\Delta E_b = E_{b1} - E_{b2}$, considering the samples with concentrations higher than 0.5 wt % and the temperature conditions where the shoulders are detectable, is around (160 ± 30) meV. This is in the energy range of the most intense vibrational modes observed by Raman spectroscopy in MEH-PPV conjugated polymer.[27,29] In the case of 0.5 wt % (Fig. 3) the E_{b2} shoulder contributes effectively to the final shape of the spectrum at 12 K, resulting in a variation of the E_{00} peak to lower energies. This explains why the E_{00} position for the 0.5 wt % case does not align with the dashed curve in the Figure 1(b). For the other spectra with concentrations higher than 0.5 wt % [Fig. 1(a)] the shoulders also appear but with lower intensities, without disturbing so much the E_{00} energy position. It is worth mentioning that the PL spectra for a pure MEH-PPV spin-casting sample are similar to those obtained for the self-sus-

Figure 3 Sequence of PL spectra at different temperatures from 295 to 12 K for the self-sustained film at 0.5 wt %. The temperatures of the spectra are 295 K, 275 K down to 25 K in steps of 25 and 12 K. The dashed lines indicate qualitatively the change of the energy positions for the pure electronic transition peak E_{00} and for the shoulders E_{b1} and E_{b2}. The shoulder appearing around 1.8 eV is the first vibronic band E_{01}.

tained films at higher MEH-PPV concentrations, concerning the shape and the energy positions of the E_{00} peak and its vibronic structure. This shows that the TPU matrix does not disturb the emission properties of the conjugated polymer inside the domains at high concentrations. The blue shift effect is probably specific for the MEH-PPV/TPU blends, it was not observed, for example, in blends of TPU and P3HT [poly(3-hexylthiphene)].[21] However, the choice of the TPU as a matrix was made because this material enables the formation of self-sustained films that can be stretched and molded and does not present any emission properties. Actually, this material offers a real possibility of development of totally polymeric devices that can be adjusted to curved surfaces and also for producing distributed feedback laser (DFB) structures. It can be molded from a solid periodic pattern, is self-sustained and can be blended with different conjugated polymers. The reproducibility of periodic DFB structures would then be possible and made at very low cost. A more extensive discussion about the morphological and optical properties of these MEH-PPV/TPU films was reported in Ref. 30. The spectrum for the self-sustained film with 0.1 wt % of MEH-PPV, however, runs completely out of the shape of all other spectra. The E_{b2} falls in the region of the E_{00} peak. The E_{00} position in this case presents the highest blue shift. These facts contribute effectively to broaden the spectrum [Fig. 1(a,c)], making the energy positions of E_{b2} and E_{00} to not have good resolution. We can only use the second derivative to find them as a trend for a more qualitative analyses. We note, however, that the energy difference of 170 meV between E_{00} (2.080 eV) and its first vibronic band E_{01} (1.910 eV) [Fig. 1(c)] remains inside the energy range of the more effective MEH-PPV vibrational modes. The energy difference $\Delta E_b = E_{b1} - E_{b2}$ in this case increases much more when compared with the other samples. It is worth to mention that at lower MEH-PPV concentration, particularly at 0.5 wt % and mainly at 0.1 wt %, the Raman intensities of the vibrational modes from the TPU material enhance substantially in comparison with the MEH-PPV vibrational modes.[30] It is possible that the TPU vibrational modes are taking place in the interaction with the π-electrons of the MEH-PPV molecules at the interfaces of the domains, contributing even more to the broadening of the E_{b2} shoulder, and, consequently, to the final shape of the spectrum.

There is not a straightforward explanation of why the shoulder E_{b1} and its first vibronic band E_{b2} appear at higher energies. This is interpreted as caused by the emission from smaller conjugation length segments of the MEH-PPV molecules formed via interactions with the TPU molecules at the interfaces of the MEH-PPV domains in the TPU matrix.
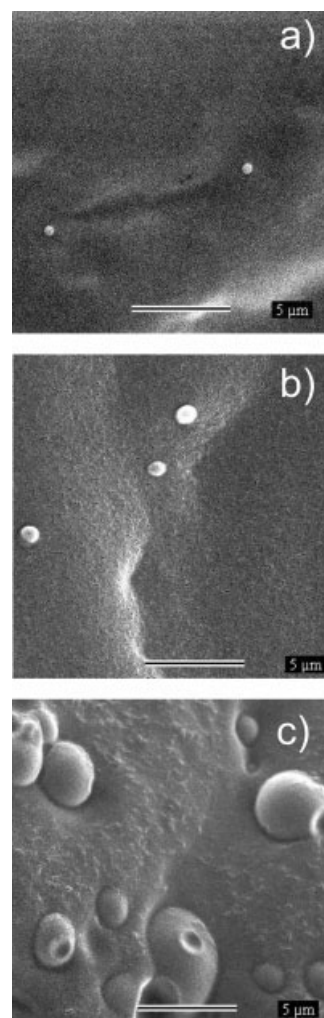
Figure 4 SEM images of MEH-PPV/TPU self-sustained films of the blends at concentrations of (a) 0.1 wt %; (b) 1.0 wt %, and (c) 10.0 wt %. The bar at the bottom of each figure represents the size scale (5 μm) of the image. The continuous phase (darker gray and gray regions) is associated to the TPU matrix and the spherical like domains to the phase rich in MEH-PPV conjugated polymer.

The formation of MEH-PPV domains in the TPU matrix was observed from SEM images, as is shown in Figure 4. Considering the origin of E_{b1} and E_{b2}, as mentioned above, it is expected that their energies would be higher.[27] We would then assign the origin of the emission spectra consisting of the E_{00} and its vibronic band E_{01} to the emission of higher conjugation length molecules inside the MEH-PPV domains. As observed in Figures 2 and 3 the shoulder E_{b1} does not change. Its energy position is practically independent of the temperature and the MEH-PPV concentration (the evolution of the PL spectra with decreasing temperature for the higher MEH-PPV concentrations are not shown for the sake of space reduction). This indicates that its origin is the same for all samples. The interactions should then occur

in all levels of concentrations, causing an effective decrease in the average conjugation length of the MEH-PPV molecules at the interfaces of the domains. The lower the conjugation length, the higher is the localization of the π-electron and, consequently, the higher is the π-electron-vibrational mode interaction in the MEH-PPV molecules, or possibly, the π-electron interaction with vibrational modes of the TPU molecules at the interfaces. For the largest domains (highest MEH-PPV concentrations), however, the amount of internal MEH-PPV molecules prevails under those at the interfaces. This explains the highest E_{00} peak intensities and why they are not disturbed by the intensity of the E_{b2} vibronic shoulder. At lower MEH-PPV concentrations (lower average volume of the MEH-PPV domains), on the other hand, the relatively higher number of molecules at the interfaces would account for a higher contribution to the emission with respect to the number of molecules inside the domains. Thus, a possibility to explain the relative increase of the intensity of E_{b2} vibronic shoulder [Fig. 1(a)] would be the decrease of the average size of the domains with decreasing the MEH-PPV concentration. In Figure 4 is shown the SEM images of the self-sustained films at concentrations of 0.1, 1.0, and 10.0 wt % of MEH-PPV in TPU. All samples have presented the morphology of spherical aggregates distributed in a matrix. The continuous phase, represented by the darker gray and gray regions, is associated to the TPU matrix and the spherical-like domains to the phase rich in MEH-PPV conjugated polymer. The average diameter of the circular domains decreases with decreasing MEH-PPV concentration. This favors the assumptions that for small MEH-PPV volumes the emission from the molecules at the interfaces represents a large contribution compared with the emission from the molecules of the central core of the domains, and also the relative increase in the intensity of E_{b2}, due to a more effective electron-vibrational mode interaction at the interfaces. Another explanation for the origin of the E_{b1} and E_{b2} shoulders could be the dilution of MEH-PPV molecules or bundles of MEH-PPV molecules, with small conjugation length, in between the MEH-PPV domains into the TPU matrix. The SEM technique does not have the required resolution to identify molecules or bundles of MEH-PPV molecules. Furthermore, the TPU characteristics, such as the glass transition, did not show changes with conjugated polymer addition, as reported in our previous work.[30] SEM images only put in evidence the presence of the MEH-PPV domains. However, if the dilution of the molecules or the bundles of MEH-PPV molecules were really effective into the TPU, the E_{b1} and E_{b2} shoulders would have their emission intensities comparable with the E_{00} peak. This would

be mainly observed for the self-sustained samples with higher MEH-PPV concentrations, which did not correspond to the respective PL spectra in Figure 1(a). In previous results, spin-casting films of poly-3-hexyl-thiophene(P3HT)/TPU blends, produced with different P3HT concentrations, were analyzed by atomic force microscopy (AFM).[21] The AFM images showed equally the formation of P3HT circular domains. The ratio between the corresponding areas of the P3HT and TPU phases matched in a good agreement with the nominal concentrations. In other words, any or a very small part of the conjugated polymer has been diluted into the TPU matrix. The same was observed for the spin-casting samples produced from the same MEH-PPV/TPU blend solutions as the self-sustained samples analyzed here. The results concerning the morphological properties of spin-casting MEH-PPV/TPU films are found in Ref. 31.

The observed blue shift of the E_{00} peak [Fig. 1(b)] is in turn attributed to a conformational problem of the MEH-PPV molecules inside the domains. The decrease of the average size of the domains favors the formation of internal MEH-PPV molecules with a lower structural ordering. Note in Figure 4 that for the blended film with 0.1 wt % of MEH-PPV the average domain size reaches the submicrometric range. This induces a decrease in their average conjugation length, leading to the blue shift of E_{00}, as observed experimentally. It is worth to mention that the blue shift of the E_{00} peak with decreasing MEH-PPV concentration was also observed at room temperature,[30] and, however, is not related to any thermal phase transition.

CONCLUSIONS

Self-sustained cast films of MEH-PPV/TPU blend material have been investigated at different concentrations. The formation of spherical-like domains of MEH-PPV into the TPU host matrix was observed from SEM images. This morphology arises from the self-organization on the heterogeneous blend. The average diameter and/or the average interfacial area of the domains decrease with decreasing MEH-PPV concentration. The PL spectra at low temperatures put in evidence the presence of two shoulders, labeled as E_{b1}, and its first vibronic band E_{b2}, at higher energy positions. Their origin is the emission from smaller conjugation length segments of the MEH-PPV molecules formed via interactions with the TPU molecules at the interfaces of the MEH-PPV domains. In addition, the amount of low conjugation length molecules at the interfaces, relatively to the amount of molecules inside the domains, will contribute effectively to the emission or to the final PL shape of the spectra with decreasing MEH-PPV concentration, as has been observed experimentally. Part of the PL spectra formed by the pure electronic tran-

sition peak E_{00} and its vibronic band E_{01} comes from the emission of the MEH-PPV molecules from inside the domains. The observed blue shift of the E_{00} peak with decreasing MEH-PPV concentration is attributed to a conformational effect. The internal MEH-PPV molecules will present a smaller average conjugation length caused by the higher structural disorder.

Our results have contributed to the understanding of the physical properties of this new blend material, which presents many advantages such as the formation of self-sustained films that can be stretched and molded. Therefore, the overall properties of the MEH-PPV/TPU blends can be considered as potentially interesting to the development of electro-optical devices.

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